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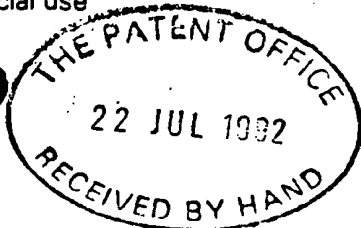
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Form 1/77

Patents Act 1977

1 Title of invention

- 1 Please give the title of the invention REFRIGERATION LUBRICANTS

2 Applicant's details

☐ First or only applicant

- 2a If you are applying as a corporate body please give:

Corporate name IMPERIAL CHEMICAL INDUSTRIES PLC

Country (and State of incorporation, if appropriate) UNITED KINGDOM

- 2b If you are applying as an individual or one of a partnership please give in full:

Surname

Forenames

- 2c In all cases, please give the following details:

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Country UNITED KINGDOM

ADP number (if known) 935003

2d, 2e and 2f: If there are further applicants please provide details on a separate sheet of paper.

☐ **Second applicant (if any)**

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please give details below

Agent's name DEE, IAN MARK

Agent's address Legal Department: Patents
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Agent's ADP number 5530647001

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② Claiming an earlier application date

5 Are you claiming that this application be treated as having been filed on the date of filing of an earlier application?

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☐ and the Section of the Patents Act 1977 under which you are claiming:

15(4) (Divisional) ☐ 8(3) ☐ 12(6) ☐ 37(4) ☐

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Continuation sheets for this Patents Form 1/77

Claim(s)

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Description

21

Abstract

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Patents Form 9/77 – Preliminary Examination/Search

Patents Form 10/77 – Request for Substantive Examination

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- 1 -

REFRIGERATION LUBRICANTS

The present invention relates generally to lubricants and more particularly to working fluid compositions contained in heat transfer devices which comprise the lubricant and a heat transfer fluid.

Heat transfer devices of the mechanical recompression type such as those used in refrigerators, freezers, heat pumps and automobile air conditioning systems are well known. In such devices a heat transfer fluid of a suitable boiling point evaporates at low pressure taking heat from a surrounding zone. The resulting vapour is then compressed and passes to a condenser where it condenses and gives off heat to a second zone. The condensate is then returned through an expansion valve to the evaporator so completing the cycle. The mechanical energy required for compressing the vapour and pumping the fluid is provided by, for example, an electric motor or an internal combustion engine.

The heat transfer fluids used in these heat transfer devices include chlorine containing fluoroalkanes such as dichlorodifluoromethane (R-12), chlorodifluoromethane (R-22) and mixtures thereof with, for example, fluoroalkanes such as 1,1-difluoroethane (R-152a). However, such chlorine containing fluoroalkanes have been implicated in the destruction of the ozone layer and as a result the use and production thereof is to be severely limited by international agreement. The use of certain fluoroalkanes and hydrofluoroalkanes in place of the chlorine containing fluoroalkanes has been proposed. The fluoroalkanes and hydrofluoroalkanes of particular interest are those compounds which have comparable

boiling points and other thermal properties to the chlorine containing fluoroalkanes which they are replacing, but which are also less damaging or benign to the ozone layer. Thus, R-12 is generally being
5 replaced by a new refrigerant, 1,1,1,2-tetrafluoroethane (R-134a).

Hitherto, heat transfer devices have tended to use mineral oils as lubricants. The good solubility of chlorine containing fluoroalkanes with mineral oils
10 allows the mineral oil to circulate around the heat transfer device together with the chlorine containing fluoroalkane, and this in turn ensures proper lubrication of the compressor. Unfortunately, however, the replacement fluoroalkane and hydrofluoroalkane heat
15 transfer fluids have different solubility characteristics to the chlorine containing fluoroalkanes presently in use and tend to be insufficiently soluble in mineral oils to allow the latter to be used as lubricants. For example,
20 1,1,1,2-tetrafluoroethane is insoluble in and hence incompatible with mineral lubricating oils. Consequently, numerous alternative lubricants such as polyoxyalkylene glycols terminating in hydroxyl and other groups, esters of polyols with mono- and
25 polyfunctional acids, and halo substituted esters and ethers have been proposed as lubricants for use with the replacement heat transfer fluids.

Unfortunately, R-134a cannot be used as a direct replacement for certain of the refrigerants which are
30 presently in use such as R-22 and R-502 (an azeotropic mixture of R-22 and chloropentafluoroethane R-115) since it does not possess comparable boiling characteristics and thermal properties. It has thus been proposed that existing refrigerants such as R-22

and R-502 be replaced by refrigerant mixtures comprising two or more refrigerants selected from the fluoroalkanes and hydrofluoroalkanes. Particular mention may be made of binary mixtures of refrigerants such as R-134a and difluoromethane (R-32) or R-32 and pentafluoroethane (R-125). Unfortunately, these refrigerant mixtures are also not sufficiently soluble in mineral oils to allow the latter to be used as lubricants. Moreover, the miscibility and solubility of an alternative lubricant with one component of the mixture, for example with R-134a, does not mean that such a lubricant will also be miscible and soluble with the refrigerant mixture itself. In consequence, the development of a lubricant which exhibits acceptable lubricating properties in a heat transfer device utilising a refrigerant mixture presents a very real problem.

It has now been found that if a prospective lubricant is at least partially soluble in each component of the refrigerant mixture then it will be at least partially soluble in the refrigerant mixture itself, thereby enabling its use as a lubricant with that mixture. Such a lubricant may provide an acceptable lubricating action even if it is immiscible with one or more of the components of the refrigerant mixture or with the refrigerant mixture itself.

According to the present invention there is provided a working fluid composition comprising (A) a heat transfer fluid comprising a mixture of at least two compounds selected from the group consisting of hydrofluoroalkanes and fluoroalkanes; and (B) sufficient to provide lubrication of a lubricant which is at least partially soluble in each component of the heat transfer fluid.

The heat transfer fluid may comprise two, three or more components. Preferred hydrofluoroalkanes and fluoroalkanes are selected from the group consisting of difluoromethane (R-32), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), 1,1-difluoroethane (R-152a), 1,1,1-trifluoroethane (R-143a) and 1,1,2-trifluoroethane (R-143).

The present invention is particularly concerned with the provision of a working fluid composition which provides a useful replacement for the working fluids presently in use which comprise R-22 or R-502 as the refrigerant and a mineral oil lubricant. A particularly desirable working fluid composition in this respect is one which comprises

(A) a heat transfer fluid comprising a mixture of:

(1) tetrafluoroethane;

(2) at least one hydrofluoroalkane selected from the group consisting of difluoromethane (R-32) and 1,1,1-trifluoroethane (R-143a); and optionally

(3) pentafluoroethane (R-125); and

(B) sufficient to provide lubrication of a lubricant which is at least partially soluble in each component of the heat transfer fluid.

The tetrafluoroethane may be 1,1,1,2-tetrafluoroethane (R-134a) or 1,1,2,2-tetrafluoroethane (R-134) or a mixture of these two isomers. Preferably, however, the tetrafluoroethane is a single isomer, and more preferably is R-134a.

Although the heat transfer fluid may comprise more than three components, it is preferably a binary or ternary mixture. The mixture may be an azeotrope or near-azeotrope, but will normally be zeotropic.

In one preferred embodiment of the present invention, the heat transfer fluid is a binary mixture of R-134a and R-32. Such a mixture provides a particularly suitable replacement for the R-22 refrigerant which has been used hitherto in commercial refrigeration systems and related heat transfer devices. Preferably, such a mixture comprises from 45 to 75 % by weight, more preferably from 65 to 75 % by weight of R-134a and the complementary percentage by weight of R-32. A particularly preferred binary mixture comprises about 70 % by weight of R-134a and about 30 % by weight of R-32.

In a further preferred embodiment of the present invention, the heat transfer fluid comprises a ternary or higher mixture of:

- (1) R-134a or R-134;
- (2) at least one hydrofluoroalkane selected from the group consisting of R-32 and R-143a; and optionally
- (3) R-125.

Such a heat transfer fluid provides a suitable replacement for the R-22 and R-502 refrigerants which have been used hitherto in commercial refrigeration systems and related heat transfer devices.

Particularly suitable ternary heat transfer fluids may be selected from:

- (a) R-134a + R-32 + R-143a;
- (b) R-134 + R-32 + R-143a;
- (c) R-134a + R-32 + R-125;
- (d) R-134 + R-32 + R-125;
- (e) R-134a + R-143a + R-125; and
- (f) R-134 + R-143a + R-125.

A particularly preferred heat transfer fluid comprises a mixture of:

- (1) R-134a or R-134, especially R-134a;

- (2) R-32 or R-143a, especially R-32; and
- (3) R-125.

Such heat transfer fluids provide a particularly suitable replacement for R-22 and R-502.

5 One particularly preferred ternary heat transfer fluid for replacing R-22 is a mixture consisting of:

- (1) 55 to 65 % by weight, particularly about 60 % by weight of R-134a;
- 10 (2) 25 to 35 % by weight, particularly about 30 % by weight of R-32; and
- (3) 5 to 15 % by weight, particularly about 10 % by weight of R-125.

 Another particularly preferred ternary heat transfer fluid for replacing R-22 is a mixture
15 consisting of:

- (1) 25 to 35 % by weight, particularly about 30 % by weight of R-134a;
- (2) 45 to 55 % by weight, particularly about 50 % by weight of R-32; and
- 20 (3) 15 to 25 % by weight, particularly about 20 % by weight of R-125.

One particularly preferred ternary heat transfer fluid for replacing R-502 is a mixture consisting of:

- 25 (1) 45 to 55 % by weight, particularly about 50 % by weight of R-134a;
- (2) 25 to 35 % by weight, particularly about 30 % by weight of R-32; and
- (3) 15 to 25 % by weight, particularly about 20 % by weight of R-125.

30 Another particularly preferred ternary heat transfer fluid for replacing R-502 is a mixture consisting of:

- (1) 45 to 55 % by weight, particularly about 50 % by weight of R-134a;

(2) 35 to 45 % by weight, particularly about 40 % by weight of R-32; and

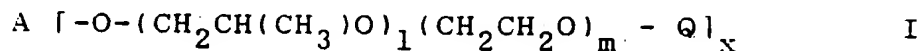
(3) 5 to 15 % by weight, particularly about 10 % by weight of R-125.

5 All the percentages by weight quoted above are based on the total weight of the ternary heat transfer fluid.

Suitable lubricants may be selected from those currently used with R-134a provided that the
10 requirement of partial solubility is met.

Lubricants satisfying the requirement of partial solubility may, in particular, be selected from the class known in the art as polyoxyalkylene glycols. Suitable polyoxyalkylene glycol lubricants include
15 hydroxyl group initiated polyoxyalkylene glycols, e.g. ethylene and/or propylene oxide oligomers/polymers initiated on mono- or polyhydric alcohols such as methanol, butanol, pentaerythritol and glycerol. Such polyoxyalkylene glycols may also be end-capped with
20 suitable terminal groups such as alkyl, e.g. methyl groups.

A preferred polyoxyalkylene glycol lubricant is one having an average molecular weight in the range of from about 150 to about 3000 and comprising one or more
25 compounds of general formula:



30 wherein

A is the residue remaining after removing the hydroxyl groups from a hydroxyl containing organic compound;

Q represents an optionally substituted alkyl, aralkyl or aryl group;

l and m are independently 0 or an integer provided that at least one of l or m is an integer; and

5 x is an integer.

The polyoxyalkylene glycol lubricant may be prepared using conventional techniques. Such techniques are well known to those skilled in the art. Thus, in one method a hydroxyl containing organic compound such
10 as an alcohol is reacted with ethylene oxide and/or propylene oxide to form an ethylene oxide and/or propylene oxide oligomer/polymer containing terminal hydroxyl groups which is subsequently etherified to give a polyoxyalkylene glycol of Formula I. The
15 polyoxyalkylene glycol lubricant which is finally formed will not usually consist of a single compound of Formula I, but will usually comprise a mixture of such compounds which vary from one another in respect of the degree of polymerisation, i.e. the number of ethylene
20 and/or propylene oxide residues. Moreover, a mixture of alcohols and/or phenols may be used as initiators in the formation of the polyoxyalkylene glycol lubricant, and a mixture of etherifying agents which provide different Q groups may also be used. The molecular
25 weight of a polyoxyalkylene glycol lubricant comprising a mixture of compounds of Formula I will represent the average molecular weight of all the compounds present, so that a given lubricant may contain specific polyoxyalkylene glycols which have a molecular weight
30 outside the range quoted above, providing that the average molecular weight of all the compounds is within that range.

The moiety A in the polyoxyalkylene glycol of Formula I is the residue remaining after removing the

hydroxyl groups from a hydroxyl containing organic compound. Such compounds include the mono- and polyhydric alcohols and phenols. Where the hydroxyl containing organic compound which is used as an initiator in the formation of the polyoxyalkylene glycol is a monohydric alcohol or phenol, A is preferably a hydrocarbyl group and more preferably is an alkyl, aryl, alkaryl or aralkyl group, especially alkyl. Suitable alkyl groups for A may be selected from the straight chain (linear), branched or cyclic alkyl groups. Preferably, A is a C₁₋₁₂, particularly a C₁₋₁₀ and especially a C₁₋₆ alkyl group. Specific examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, the various pentyl groups, the various hexyl groups, cyclopentyl, cyclohexyl and the like. Particularly preferred alkyl groups for A are the C₁₋₁₂, particularly the C₁₋₁₀ and especially the C₁₋₆ straight chain alkyl groups, examples of which have been listed above. An especially preferred alkyl group for A is methyl or n-butyl.

Other suitable hydrocarbyl groups for A are those which remain after removing a hydroxyl group(s) from benzyl alcohol and phenols such as phenol, cresol, nonylphenol, resorcinol and bisphenol A.

Where a polyhydric alcohol is used in the formation of the polyoxyalkylene glycol, A is preferably a hydrocarbon radical. Suitable hydrocarbon radicals for A are those which remain after removing the hydroxyl groups from polyhydric alcohols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, cyclohexane dimethanol, glycerol, 1,2,6-hexane triol, trimethylolpropane, pentaerythritol, dipentaerythritol

and sorbitol. A particularly preferred hydrocarbon radical for A is that remaining after removing the hydroxyl groups from glycerol.

5 The moiety Q in the polyoxyalkylene glycol of Formula I is an optionally substituted alkyl, aralkyl or aryl group. A preferred optionally substituted aralkyl group for Q is an optionally substituted benzyl group. Preferred optionally substituted aryl groups for Q include phenyl and alkyl substituted phenyl groups.
10 Preferably, Q is an optionally substituted, for example halogen substituted, alkyl group, particularly an optionally substituted C₁₋₁₂ alkyl group and more particularly an optionally substituted C₁₋₄ alkyl group. Suitable alkyl groups for Q may be selected from
15 the straight chain (linear), branched or cyclic alkyl groups, especially the linear alkyl groups. Although the alkyl groups for Q are described as being optionally substituted, they are preferably unsubstituted. Accordingly, particularly preferred
20 alkyl groups for Q are selected from methyl, ethyl, propyl, isopropyl and the various butyl groups. An especially preferred alkyl group for Q is methyl.

 The polyoxyalkylene glycol of Formula I may be a polyoxyethylene glycol, a polyoxypropylene glycol or a
25 poly(oxyethylene/oxypropylene) glycol. In the latter case, the ethylene and propylene oxide residues may be arranged randomly or in blocks along the polymer chain. Preferred polyoxyalkylene glycols are the polyoxypropylene glycols and the
30 poly(oxyethylene/oxypropylene) glycols.

 Particularly preferred lubricants for use in the working fluid compositions of the invention are those selected from the class known as neopentyl polyol esters. Suitable neopentyl polyol esters include the

esters of pentaerythritol, polypentaerythritols such as di- and tripentaerythritol, trimethylol alkanes such as trimethylol ethane and trimethylol propane, and neopentyl glycol. Such esters may be formed with linear
 5 and/or branched aliphatic carboxylic acids, such as linear and/or branched alkanoic acids, or esterifiable derivatives thereof. A minor proportion of an aliphatic polycarboxylic acid, e.g. an aliphatic dicarboxylic acid, or an esterifiable derivative thereof may also be
 10 used in the synthesis of the ester lubricant in order to increase the viscosity thereof. However, where such an aliphatic polycarboxylic acid (or esterifiable derivative thereof) is employed in the synthesis, it will preferably constitute no more than 30 mole %, more
 15 preferably no more than 10 mole % of the total amount of carboxylic acids (or esterifiable derivatives thereof) used in the synthesis. Usually, the amount of the carboxylic acid(s) (or esterifiable derivative thereof) which is used in the synthesis will be
 20 sufficient to esterify all, or substantially all, of the hydroxyl groups contained in the polyol, but in certain circumstances residual hydroxyl functionality may be acceptable.

A preferred neopentyl polyol ester lubricant is
 25 one comprising one or more compounds of general formula:



30

wherein

R is the hydrocarbon radical remaining after removing all, or substantially all, of the hydroxyl groups from pentaerythritol, dipentaerythritol.

tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol, or the hydroxyl containing hydrocarbon radical remaining after removing a proportion of the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol;

each R^1 is independently H, a straight chain (linear) aliphatic hydrocarbyl group, a branched aliphatic hydrocarbyl group, or an aliphatic hydrocarbyl group (linear or branched) containing a carboxylic acid or carboxylic acid ester substituent, provided that at least one R^1 group is a linear aliphatic hydrocarbyl group or a branched aliphatic hydrocarbyl group; and

n is an integer of at least 2.

The aliphatic hydrocarbyl groups specified for R^1 above may be substituted, e.g. by pendant atoms or groups such as chloro, fluoro and bromo, and/or by in chain hetero atoms such as oxygen and nitrogen. Preferably, however, such hydrocarbyl groups are unsubstituted and, except in the case where R^1 is an aliphatic hydrocarbyl group containing a carboxylic acid or carboxylic acid ester substituent, contain only carbon and hydrogen atoms.

The ester lubricants of Formula II may be prepared by reacting the appropriate polyol or mixture of polyols with the appropriate carboxylic acid or mixture of acids. Esterifiable derivatives of the carboxylic acids may also be used in the synthesis, such as the acyl halides, anhydrides and lower alkyl esters thereof. Suitable acyl halides are the acyl chlorides and suitable lower alkyl esters are the methyl esters. Aliphatic polycarboxylic acids, or esterifiable derivatives thereof, may also be used in the synthesis

of the ester lubricant. Where an aliphatic polycarboxylic acid is used in the synthesis of the ester lubricant, the resulting lubricant will comprise one or more compounds of Formula II in which at least one of the R^1 groups is an aliphatic hydrocarbyl group (linear or branched) containing a carboxylic acid or carboxylic acid ester substituent. The ability of polycarboxylic acids to react with two or more alcohol molecules provides a means of increasing the molecular weight of the ester formed and so a means of increasing the viscosity of the lubricant. Examples of such polycarboxylic acids include maleic acid, adipic acid and succinic acid, especially adipic acid. Generally, however, only monocarboxylic acids (or esterifiable derivatives thereof) will be used in the synthesis of the ester lubricant, and where polycarboxylic acids are used they will be used together with one or more monocarboxylic acids (or esterifiable derivatives thereof) and will constitute only a minor proportion of the total amount of carboxylic acids used in the synthesis. Where an aliphatic polycarboxylic acid (or an esterifiable derivative thereof) is employed in the synthesis, it will preferably constitute no more than 30 mole %, more preferably no more than 10 mole % of the total amount of carboxylic acids used in the synthesis, with one or more monocarboxylic acids (or esterifiable derivatives thereof) constituting the remainder.

Usually, the amount of the carboxylic acid(s) (or esterifiable derivative thereof) which is used in the synthesis will be sufficient to esterify all, or substantially all, of the hydroxyl groups contained in the polyol(s), in which case R in the above Formula II is the hydrocarbon radical remaining after removing

all, or substantially all, of the hydroxyl groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol. However, in certain circumstances ester
5 lubricants which comprise residual hydroxyl functionality may be acceptable. Such lubricants comprise one or more ester compounds of Formula II in which R is the hydroxyl containing hydrocarbon radical remaining after removing a proportion of the hydroxyl
10 groups from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylol ethane, trimethylol propane or neopentyl glycol. Esters containing residual (unreacted) hydroxyl functionality are often termed partial esters, and lubricants containing them may be
15 prepared by utilising an amount of the carboxylic acid or acids which is insufficient to esterify all of the hydroxyl groups contained in the polyol or polyols.

It will be appreciated that the preferred neopentyl polyol ester lubricants may comprise a single
20 compound of Formula II, i.e. the reaction product which is formed between a single polyol and a single monocarboxylic acid. However, such ester lubricants may also comprise a mixed ester composition comprising two or more compounds of Formula II. Such mixed ester
25 compositions may be prepared by utilising two or more polyols and/or two or more carboxylic acids (or esterifiable derivatives thereof) in the synthesis of the ester, or by combining a mixture of different esters each of which is the reaction product of a
30 particular polyol and a particular carboxylic acid. Furthermore, different mixed ester compositions, each of which has been prepared by utilising two or more polyols and/or two or more carboxylic acids (or

esterifiable derivatives thereof) in their synthesis, may also be blended together.

5 The preferred neopentyl polyol ester lubricants comprise one or more compounds of Formula II in which R is the hydrocarbon radical remaining after removing all, or substantially all, of the hydroxyl groups from pentaerythritol, dipentaerythritol, trimethylol propane or neopentyl glycol. Particularly preferred alcohols for the synthesis of the ester are pentaerythritol, 10 dipentaerythritol and trimethylol propane.

Preferably, each R^1 in Formula II is, independently, a linear aliphatic hydrocarbyl group or a branched aliphatic hydrocarbyl group.

15 Preferred linear aliphatic hydrocarbyl groups for R^1 are the linear alkyl groups, particularly the C_{3-10} linear alkyl groups, more particularly the C_{5-10} linear alkyl groups and especially the C_{5-8} linear alkyl groups. Examples of suitable linear alkyl groups include n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl 20 and n-decyl. Esters containing such alkyl groups can be prepared by utilising a linear alkanolic acid in the synthesis of the ester.

Preferred branched aliphatic hydrocarbyl groups for R^1 are the branched alkyl groups, particularly the 25 C_{4-14} branched alkyl groups, more particularly the C_{6-12} branched alkyl groups and especially the C_{8-10} branched alkyl groups. Examples of suitable branched alkyl groups include isopentyl, isohexyl, isoheptyl, isooctyl, isononyl, isodecyl, 2-ethylbutyl, 30 2-methylhexyl, 2-ethylhexyl, 3,5,5-trimethylhexyl, neopentyl, neoheptyl and neodecyl. Esters containing such alkyl groups can be prepared by utilising a branched alkanolic acid in the synthesis of the ester.

In a particularly preferred embodiment of the present invention, the ester lubricant comprises one or more compounds of general formula:



wherein

10 R^2 is the hydrocarbon radical remaining after removing all, or substantially all, of the hydroxyl groups from pentaerythritol, dipentaerythritol or trimethylol propane;

each R^3 is independently a linear alkyl group or a
15 a branched alkyl group; and

n is an integer of 3, 4 or 6,

wherein one or more of the named polyols, one or more linear alkanolic acids, or esterifiable derivatives thereof, and optionally one or more branched alkanolic
20 acids, or esterifiable derivatives thereof, are utilised in the synthesis of the ester lubricant.

Preferably, a mixture of two or more linear alkanolic acids, in particular two, or esterifiable derivatives thereof, are utilised in the synthesis of
25 the ester lubricant of Formula III. More preferably, a mixture of one or more linear alkanolic acids, or esterifiable derivatives thereof, and one or more branched alkanolic acids, or esterifiable derivatives thereof, are utilised in the synthesis. Thus,
30 particularly preferred ester lubricants of the invention are mixed ester compositions which comprise a plurality of compounds of Formula III.

Where a mixture of linear and branched alkanolic acids (or esterifiable derivatives thereof) are

utilised in the synthesis of the ester lubricant, as is preferred, the linear alkanolic acid(s) preferably constitutes at least 25 mole %, e.g from 25 to 75 mole %, of the total amount of carboxylic acids used.

5 In this way, at least 25 mole %, e.g. from 25 to 75 mole %, of the hydroxyl groups contained in the polyol or mixture of polyols may be reacted with the said linear alkanolic acid(s).

10 Ester lubricants comprising one or more compounds of Formula III provide a particularly good balance between the properties desired of a lubricant and, in particular, exhibit good thermal stability, good hydrolytic stability and acceptable solubility and miscibility with the heat transfer fluid. As stated
15 previously, the present invention is particularly concerned with the provision of a working fluid composition which can replace the existing working fluid compositions comprising R-22 or R-502 as the refrigerant. Refrigeration systems which contain
20 replacements for R-22 and R-502 typically operate at temperatures above those using R-134a as the sole replacement refrigerant. Thus, it is particularly desirable that the lubricant which is used in a working fluid composition designed to replace the existing
25 compositions based on R-22 and R-502 exhibits good thermal stability.

Preferably, R^2 is the hydrocarbon radical remaining after removing all, or substantially all, of the hydroxyl groups from pentaerythritol or
30 dipentaerythritol.

Preferred linear and branched alkyl groups for R^3 are those described above in connection with R^1 and are derived by utilising the corresponding alkanolic acids or esterifiable derivatives thereof.

An especially preferred ester lubricant is a mixed ester composition which comprises a plurality of compounds of Formula III and which is the reaction product of pentaerythritol, heptanoic acid and a mixture of branched C_{8-10} alkanolic acids. Preferably, the heptanoic acid will constitute from 25 to 75 mole % of the total amount of acids utilised in the synthesis, with the branched C_{8-10} acids constituting the remainder. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

Another especially preferred ester lubricant is a mixed ester composition which comprises a plurality of compounds of Formula III and which is the reaction product of pentaerythritol, dipentaerythritol, heptanoic acid and a branched C_9 alkanolic acid. Preferably, the heptanoic acid will constitute from 25 to 75 mole % of the total amount of acids utilised in the synthesis, with the branched C_9 acid constituting the remainder. Esterifiable derivatives of the acids may also be used in the synthesis of the ester.

The lubricant will typically be part of a lubricant composition which also comprises one or more of the additives which are conventional in the refrigeration lubricants art. Specific mention may be made of thermal stability improvers, corrosion inhibitors, metal deactivators, viscosity index improvers, anti-wear agents and extreme pressure resistant additives. Such additives are well known to those skilled in the art.

The working fluid compositions of the invention will typically comprise a major amount of the heat transfer fluid and a minor amount of the synthetic lubricant. Preferably, the working fluid compositions

of the invention will comprise from 50 to 99 % by weight, more preferably from 70 to 99 % by weight, of the heat transfer fluid and from 1 to 50 % by weight, more preferably from 1 to 30 % by weight, of the lubricant based on the total weight thereof.

The working fluid compositions are useful in all types of compression cycle heat transfer devices. Thus, they may be used to provide cooling by a method involving condensing the heat transfer fluid and thereafter evaporating it in a heat exchange relationship with a body to be cooled. They may also be used to provide heating by a method involving condensing the heat transfer fluid in a heat exchange relationship with a body to be heated and thereafter evaporating it.

The working fluid compositions of the invention provide a good compromise between performance and low or zero ozone depletion. They are especially suitable for applications currently satisfied by refrigerants R-22 and R-502.

The present invention is now illustrated, but not limited, with reference to the following examples.

In these examples various compositions were prepared comprising 15 % w/w of a lubricant and the complementary percentage of a heat transfer fluid comprising (by weight) equal proportions of R-134a and R-32. The lower miscibility temperature was determined, i.e. the lowest temperature at which the lubricant remained miscible with the heat transfer fluid. The results are displayed in Table 1, together with the lower miscibility temperature of the lubricant in each component of the heat transfer fluid. Each lubricant was at least partially soluble in each of the

components of the heat transfer fluid and also in the fluid itself.

TABLE 1

5

LUBRICANT	LOWER MISCIBILITY TEMPERATURE (°C)		
	R-134A	R-32	MIXTURE
10 PE6	<-60	0	-27
"EMKARATE" (TM) RL-212	-25	>20	-3
"EMKARATE" (TM) RL-184	10	>20	>10
"EMKAROX" (TM) RL-118	<-60	I	I

15

I - denotes immiscibility over the temperature range -50 °C to +20 °C.

PE6 is an ester of pentaerythritol and n-hexanoic acid.

20

"EMKARATE" (TM) RL-212 is a commercially available ester based lubricant for use with R-134a obtainable from ICI Chemicals & Polymers Ltd. Specifically, the lubricant comprises an ester of trimethylol propane and heptanoic acid.

25

"EMKARATE" (TM) RL-184 is a commercially available ester based lubricant for use with R-134a obtainable from ICI Chemicals & Polymers Ltd. Specifically, the lubricant comprises an ester of pentaerythritol, heptanoic acid and a mixture of branched C₈₋₁₀ alkanolic acids.

30

"EMKAROX" (TM) RL-118 is a commercially available polyoxyalkylene glycol based lubricant for use with R-134a obtainable from ICI Chemicals & Polymers Ltd.

Specifically, the lubricant comprises an end-capped polyoxyalkylene glycol.

"EMKARATE" and "EMKAROX" are trademarks of ICI Chemicals & Polymers Ltd.

5

In a further series of experiments, various compositions were prepared comprising 15 %w/w of each of the above lubricants and the complementary percentage of R-125, in which each of the lubricants is at least partially soluble. The lower miscibility temperature was again determined and the results are displayed in Table 2.

10

TABLE 2

15

LUBRICANT	LOWER MISCIBILITY TEMPERATURE	
	(^C)	
	R-125	
20 PE6	<-60	
"EMKARATE" (TM) RL-212	<-60	
"EMKARATE" (TM) RL-184	<-60	
"EMKAROX" (TM) RL-118	<-60	

25

30

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